

# **Evaluation of Small-Particle Plasma Spray for SOFC Electrolyte Deposition**

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## **Introduction**

The commercialization efforts for solid-oxide fuel cell (SOFC) systems are beginning to emphasize cost reduction in order to compete more effectively with other power generating methods. Several aspects of the SOFC stack have attracted particular attention for cost reduction efforts, with electrolyte deposition being one area of focus. Currently, SOFC electrolytes are processed using a range of methods, including tape casting methods, slurry/sol-gel, and electrochemical vapor deposition (EVD). Of these methods, tape casting is reportedly the most economical while EVD has higher costs. Atmospheric-plasma spray (APS) is likely to offer a cost competitive alternative to tape casting, but thin and dense electrolyte layers cannot be produced readily with conventional equipment. Small-particle plasma spray (SPPS) is a modified APS process which allows the deposition of thin and dense coatings by thermal spray.

## **Objective**

The objective of this project is to demonstrate the feasibility of depositing yttria-stabilized zirconia (YSZ) electrolytes onto lanthanum strontium manganite (LSM), and other test substrates. This includes characterizing the effect of process parameters and YSZ powder size on cell performance and electrolyte morphology. The goals of this effort are to demonstrate reliable deposition of dense and crack-free YSZ electrolytes on LSM by SPPS and to evaluate the performance of these electrolytes on both planar and tubular cathodes

## **Approach**

The initial tasks of the program were to demonstrate a preheat cycle which would allow deposition of YSZ onto LSM,

and screening of the deposition parameters using Hastelloy C substrates. Once process parameters are developed on the planar substrates, the process will be transferred to tubular substrates provided by Westinghouse. Modification of the process parameters is expected when the process is transferred to the tubular substrates, and developmental samples will be provided to Westinghouse for evaluation.

### **SPPS Technology**

SPPS technology allows the use of very fine ( 0.2 micron or larger) discrete powders. SPPS consists of both powder injection and feed technology, and is currently in the final phases of the patent process. SPPS can be retrofitted to any commercial plasma spray gun. Through the use of fine powders, SPPS has produced dense (>98%) yttria-stabilized zirconia (YSZ) coatings as thin as 5 micron for use in electrochemical sensors. An initial demonstration of SPPS for SOFC fabrication successfully produced SOFC tri-layers for electrochemical testing which resulted in an open circuit voltage approximately 80% of the theoretical value.

### **Results**

In previous efforts to document the characteristics of SPPS for thick (25 micron to 100 micron) films, deposition rates of up to 5.5 pounds per hour of 5 micron  $\text{Al}_2\text{O}_3$  and a deposition efficiency of approximately 65% were measured. For this effort, coating thicknesses of 15 to 20 micron were targeted and tests performed to characterize the process for producing thin films. Producing thinner films requires a slower powder feed rate and the use of finer powder. Using the 3 micron YSZ, coating rates between 0.13 to 0.60 microns/pass were studied.

For initial screening of deposition parameters, disk substrates approximately 1.5 cm in diameter were used. Hastelloy C substrates were selected solely because of their ready availability. LSM substrates were prepared by uniaxially pressing and then sintering. Two substrate heaters were evaluated for the LSM substrate; one with a maximum temperature of 850°C while the other was capable of 1200°C. Disks of LSM were heated to a selected temperature, and then the thermal gun was cycled across the face of the sample at the expected deposition conditions. After exposure, the disks were visually inspected for damage. Preheat temperatures above 900°C were found to be suitable, and the substrate holder is being modified for this temperature regime.

Using the Hastelloy C substrates, a basic set of plasma spray parameters were investigated in the first phase of experiments. Initial coatings were deposited on thermal shock resistant 26% porous Hastelloy substrates. The substrates were cleaned by sequential immersion in acetone and isopropanol in an ultrasonic bath. The back of the substrates were exposed to Argon during the coating process to reduce oxidation. YSZ coatings were deposited by a robot controlled plasma spray system (Plasma Technik A-3000S). Eight mole % YSZ powder (Advanced Technology Powders) with a 3.0 micron particle size was used in all experiments. The spray distance was kept constant at 5 cm and the substrate was preheated with five passes of the plasma gun. The plasma power, hydrogen flow rate, powder feed rate, injector parameters, and plasma gun traverse speed were selectively varied.

Coatings deposited at the lowest plasma power (36.5 kW) showed no indication of unmelted particles in the microstructures and a low fraction of porosity. Increased plasma power (45.5 kW), however, produced coatings with finer porosity. Modifying the injector parameters significantly reduced the coating porosity and increased the deposition rate twofold. The powder feed rates and hydrogen flow rates examined in this study did not significantly influence the coating morphology. However, high plasma power with low powder feed rates yielded coatings with excellent conformal coverage as the molten splat was able to spread over the porous substrate surface. Slowing the gun traverse speed from 350 mm/s to 245 mm/s, and, thereby, the plasma residence time, created both lateral and longitudinal cracks in the coatings while only slightly increasing the deposition rate. In addition, a greater amount of substrate oxidation occurred.

Scanning electron microscopy (SEM) was performed on polished cross sections of the samples. Very little difference in the microstructure of the YSZ coatings was observed, with all of the coatings showing evidence of grain pullout and small amounts of porosity. The YSZ coatings adhered well to the Hastelloy substrates and no delamination was observed. Inspection of the coatings revealed good thickness uniformity and no evidence of intergranular cracking was observed at the magnifications used (2 kX). With the Hastelloy substrate serving as an anode, silver paste cathodes were attached to samples with promising cell microstructures and the open circuit voltage evaluated at 750°C with air and 3% H<sub>2</sub> - 97% Ar at the respective electrodes. Cell tests samples were fabricated by first depositing a YSZ coating at low powder feed rate to obtain good surface conformal coverage, and then building up the YSZ layer at higher powder feed rates. SEM showed the coatings to be approximately 50 microns thick with

a high visible density. These cells displayed an open circuit voltage of 80% theoretical.

### **Application**

In addition to SOFC electrolyte fabrication, SPPS is also being evaluated for the formation of advanced thermal barrier coatings within the AGTSR program, the replacement of hard chrome plating for corrosion protection in Naval applications (DARPA), and other membrane applications. The very high bond strength achieved with SPPS, 10 KSI with 220 or 400 grit surface preparation, coupled with the ability to produce thin and dense coatings is also creating opportunities for dielectric, wear, and metallization.

### **Future Activities**

In the next months, further development of the SPPS process will be done with a strong emphasis on the LSM substrates. Process improvement will be based on a design-of-experiments approach on the flat substrates. This process improvement effort will drive the final design of a lathe system for processing tubular LSM substrates for process demonstration. We will also continue a parallel effort on the development of spray pyrolysis as an alternative electrolyte deposition process for YSZ.

### **Acknowledgments**

This research is sponsored by Battelle - Pacific Northwest Laboratory under order# 268884-AF2 with Northwestern University, 633 Clark Street, Evanston IL 60208-1110, Telefax (847)491-4800. The project monitor at Battelle - Pacific Northwest Laboratory is Dr. T. Armstrong. The period of performance 10/96 to 9/97.